

6. CONCLUSIONS

This project was motivated by monitoring data suggesting that americium and plutonium may have migrated through one or more layers of sedimentary interbed below the SDA. Such behavior is inconsistent with traditional modeling approaches, which predict americium and plutonium mobilities in interbed to be very low and thus imply that interbed should be an effective barrier to migration. The original objective of the project was to determine if high mobility forms of plutonium could be observed in laboratory columns eluted with a perched water simulant. The simulant contained elevated, although not extreme, concentrations of potential chelating agents. As the project progressed, the scope expanded to include uranium and americium, which are important contaminants at the SDA, as well as thorium and americium, which are often cited as analogs for plutonium(IV) and plutonium(V), respectively. The objectives were also extended to attempt to provide mechanistic explanations for the observed behaviors.

Three major conclusions can be drawn regarding actinide transport under the influence of the perched water simulants used in these studies. These are as follows: (1) multiple physical/ chemical forms, each having distinctly different mobilities, are possible, (2) for time scales on the order of weeks and longer, actinide behavior is generally dominated by solid forms, and (3) high mobility forms, which differ among the actinides, are possible. The hypothesized physical/chemical forms of the contaminants are summarized in Table 6.1 and discussed below. As discussed below, these findings have important implications regarding the behavior of actinide contaminants below the SDA and the conceptual models used to predict their behavior.

Multiple physical/chemical forms, each having distinctly different mobilities, are possible: This phenomenon, which was not observed for strontium or uranium, was most pronounced for americium, thorium, and plutonium(IV) in the presence of EDTA and for neptunium in the presence and absence of EDTA. In these tests, the mobilities were characterized by a small (<1%) high mobility component with $R < 3$, a large ($\approx 50\%$) intermediate mobility component with $3 < R < 1000$, and a large ($\approx 50\%$) low mobility component with $R > 1000$. This finding has significant implications with respect to modeling because it suggests that the traditional approach of using batch distribution coefficients (K_D) to infer contaminant mobility may not be appropriate for some contaminants in some situations. The key, of course, is identifying those situations

Table 6.1. Summary of Hypothesized Physical/Chemical Forms (in the Absence of EDTA)

Radionuclide	High Mobility Component	Low Mobility Component
Americium(III)	Predominately particulate carbonate or hydroxy-carbonate species	Particulate carbonate or hydroxy-carbonate species
Thorium(IV)/ Plutonium(IV)	Hydroxide species sorbed to silica precipitates and/or polymeric oxy-hydroxide precipitates	Hydroxide species sorbed to soil matrix and/or polymeric oxy- hydroxide precipitates filtered by the soil matrix
Neptunium(V)	Soluble carbonate species	Reduced to neptunium(IV) – same species as thorium(IV)/plutonium(IV)
Plutonium(V)	Predominately particulate forms, probably plutonium(IV) species. Soluble carbonates possible.	Reduced to plutonium(IV) – same species as thorium(IV)/plutonium(IV)
Uranium(VI)	Soluble carbonate species	In the long term, likely dominated by uranium mineralization

where an alternate approach is warranted. For example, the plutonium(IV) – EDTA complex which was responsible for the intermediate mobility component in the experiments is a transient species which would only be important at the SDA in an episodic infiltration event such as a flood.

The behavior of americium, thorium, and plutonium is dominated by solid species of low mobility: In the absence of EDTA, more than 99% of the americium, thorium, and plutonium(IV) had low mobilities ($R > 1000$) in the columns. This behavior is consistent with the thermodynamic phase diagrams which predict americium to be an insoluble carbonate or hydroxy-carbonate precipitate and thorium and plutonium(IV) to either be a hydroxide or an oxy-hydroxide polymer. The behavior is also consistent with sorption to silicate precipitates as speciation modeling predicts that the groundwater simulants are oversaturated with respect to silicates. Although not obvious, the behaviors of neptunium and plutonium(V) are also likely to be dominated by solid species. The neptunium data for “oxidized” columns and for normal columns at different flow rates both suggest reduction of neptunium(V) to neptunium(IV) by the interbed. Neptunium(IV) is hydrolyzed at pH 8 and likely forms the same immobile solid species as thorium and plutonium(IV). Plutonium(V) is more easily reduced than neptunium(V), and its low mobility component was greater than 99%, both in the presence and absence of EDTA. Thus, its behavior is likely governed by its reduction to the immobile plutonium(IV). The low mobility of plutonium(V) is contingent on its encountering redox active constituents in the path of migration. This seems likely below the SDA.

In the laboratory columns uranium had high mobility ($R \approx 3$) due to the soluble complexes that it forms with carbonate. While the carbonate species are likely to control transport in the short term and would be important in episodic transport scenarios, long term transport is affected by aging processes and is likely dominated by insoluble calcium and/or phosphate mineral species. Since the solubilities of these uranium mineral species are typically much lower than the uranyl carbonates, long-term uranium mobility below the SDA is likely to be much lower than suggested by the column experiments.

High mobility forms are possible: High mobility forms were observed for americium, thorium, plutonium(IV), neptunium, and plutonium(V). The physical/chemical nature of these forms differed. Effluent filtrations showed the americium and neptunium high mobility form to be smaller than 3 nm, thorium to be larger than 3 nm, and plutonium(IV) and plutonium(V) to have portions both smaller and larger than 3 nm. When combined

with batch filtration data and speciation modeling predictions, hypotheses are advanced regarding the nature of these high mobility forms as follows: americium – americium carbonate or hydroxy carbonate in either a soluble or small (<3 nm) precipitate form; thorium – thorium oxy-hydroxide polymer or hydrolyzed thorium sorbed to silicate precipitates (>3 nm); plutonium(IV) - plutonium oxy-hydroxide polymer or hydrolyzed plutonium sorbed to silicate precipitates; neptunium – soluble neptunium carbonate; plutonium(V) – plutonium carbonate complexes and the same species as above for plutonium(IV), due to reduction of plutonium(V) to plutonium(IV).

Collectively, these results provide a plausible explanation for the apparent disconnect between the transport model, which predicts interbed to be an effective barrier for plutonium and americium migration, and field data, which indicate penetration of that barrier. They are consistent with the transport model in that the column tests also show interbed to be an effective geochemical barrier ($R > 1000$). They differ from the transport model however, in that the interbed was experimentally found to be effective for most of the americium and plutonium rather than all of it as predicted. The results are, at the same time, consistent with the field data. The high mobility forms appear to be at least partly colloidal, and the transport of colloidal material through the subsurface is likely to be stochastic. In fact, some of the breakthrough curves, particularly those for plutonium(V), not only had a high mobility component early in the test but also exhibited sporadic release of very small amounts throughout the duration of the experiment. This is consistent with the sporadic occurrence of americium and plutonium in monitoring data.

Additional findings of potential interest are the effect of mean linear velocity and the ability of the interbed matrix to attenuate colloids. Decreasing the mean linear velocity an order of magnitude below the value used in most of the tests did not affect retardation factors for any of the contaminants that were tested (neptunium, uranium, and strontium). These results provide a measure of assurance that behavior predicted by the columns may be applicable at the much lower mean linear velocities that are typical below the SDA. However, this extrapolation needs to be applied with care because there can be kinetic effects which are significant. For example, fractional recovery for neptunium declined when the flow rate was reduced because the increase in residence time provided for a greater reduction from neptunium(V) to neptunium(IV) by the soil. Similarly, the intermediate mobility fractions that resulted from EDTA complexation with americium, thorium, and plutonium(IV) were short lived. The ability of the 106 to 250 μm

size fraction to attenuate colloids smaller than 20 nm was surprising and supports the findings that there is very little penetration of interbed by the colloidal forms.

7. REFERENCES

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